University of Stuttgart
Institute for Theoretical Chemistry

Use of automated term-generation and general tensor contractions in electronic structure theory

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ESNT-Workshop
“Automated tools for many-body theory”
June 6, 2023

Motivation

Main target: Electronic Schrödinger equation for many-electron systems (molecules)

$$\left(\hat{T}_\mathrm{e} + \hat{V}_\mathrm{ne} + \hat{V}_\mathrm{ee}\right)|\Psi_\mathrm{e}\rangle = |\Psi_\mathrm{e}\rangle E_\mathrm{e}$$

Main formalism: Second quantization

$$\hat{V}_\mathrm{ee} = \frac{1}{4}\sum_{pqrs} g_{pr}^{qs}\ \hat{a}^p \hat{a}^r \hat{a}_s \hat{a}_q$$

Main ansatz for wavefunctions: $e^{\hat{T}}|\Psi_\mathrm{ref}\rangle$

Main issue: lengthy expressions

$$\begin{aligned}
&\mathcal{L}_{\mathrm{SP}} + V_i^{r''}\bar{t}_a^i + \bar{B}_i^{a''}\bar{t}_a^i - X_j^a F_i^j \bar{t}_a^i + B_i^{a''}\bar{t}_a^i + F_j^{p''}\Lambda_i^a \mathcal{R}_{ap''}^{ib}\bar{t}_b^j - F_i^{p''}\Lambda_j^a \mathcal{R}_{ap''}^{ib}\bar{t}_b^j - \Lambda_j^a G_{ik}^{jp''}\mathcal{R}_{ap''}^{ib}\bar{t}_b^k + \Lambda_i^a V_a^{b''}\bar{t}_b^i - \Lambda \\
&+ \Lambda_j^b V_{ik}^{ja}\bar{t}_b^k\bar{t}_a^i - \Lambda_j^a V_i^b t_a^i\bar{t}_b^j - G_{ik}^{ap''}\Lambda_j^b t_a^j \mathcal{R}_{bp''}^{ic}\bar{t}_c^k + G_{ik}^{ap''} t_a^i \Lambda_j^b \mathcal{R}_{bp''}^{jc}\bar{t}_c^k - G_{ij}^{ap''} t_a^i \Lambda_k^b \mathcal{R}_{bp''}^{jc}\bar{t}_c^k + \Lambda_{ij}^{ab} C_{ab}^{ic}\bar{t}_c^j + \Lambda_{ik}^{ab}(\\
&- \Lambda_{ij}^{ab} G_{ka}^{ip''}\mathcal{R}_{bp''}^{jc}\bar{t}_c^k + \Lambda_{ij}^{ab} V_{ab}^{ic}\bar{t}_c^j - F_j^{p''}\Lambda_{ik}^{ab} t_b^j \mathcal{R}_{ap''}^{ic}\bar{t}_c^k - \Lambda_{jl}^{ab} G_{ik}^{jp''} t_a^k \mathcal{R}_{bp''}^{ic}\bar{t}_c^l - \Lambda_{ij}^{ab} G_{kl}^{jp''} t_b^k \mathcal{R}_{ap''}^{ic}\bar{t}_c^l + \Lambda_{ik}^{ab} V_{ja}^{ic} t_b^j\bar{t}_c^k \\
&+ \Lambda_{jk}^{ac} G_{ia}^{bp''} t_b^j \mathcal{R}_{cp''}^{id}\bar{t}_d^k - \Lambda_{ij}^{ab} G_{kb}^{cp''} t_c^j \mathcal{R}_{ap''}^{id}\bar{t}_d^k + \Lambda_{jk}^{bc} G_{ic}^{ap''} t_a^j \mathcal{R}_{bp''}^{jd}\bar{t}_d^k + \Lambda_{ik}^{ab} V_{jl}^{kc} t_{ab}^{il}\bar{t}_c^j - \Lambda_{ik}^{ab} V_j^c t_{ab}^{ij}\bar{t}_c^k + \Lambda_{kl}^{ab} V_{ij}^{kc} t_{ab}^{ij}\bar{t}_c^l \\
&- G_{kl}^{bp''}\Lambda_{ij}^{ac} t_{ab}^{ij}\mathcal{R}_{cp''}^{kd}\bar{t}_d^l + G_{il}^{ap''}\Lambda_{jk}^{bc} t_{ab}^{ij}\mathcal{R}_{cp''}^{kd}\bar{t}_d^l - G_{ik}^{ap''}\Lambda_{jl}^{bc} t_{ab}^{ij}\mathcal{R}_{cp''}^{kd}\bar{t}_d^l - G_{ij}^{ap''}\Lambda_{kl}^{bc} t_{ac}^{ij}\mathcal{R}_{bp''}^{kd}\bar{t}_d^l + \tfrac{1}{2}\Lambda_{il}^{ab} V_{jk}^{ic} t_a^j t_b^k\bar{t}_c^l \\
&- G_{jl}^{cp''}\Lambda_{ik}^{ab} t_b^j t_c^k \mathcal{R}_{ap''}^{id}\bar{t}_d^l - G_{ij}^{bp''}\Lambda_{kl}^{ac} t_a^j t_b^k \mathcal{R}_{cp''}^{id}\bar{t}_d^l - G_{ik}^{ap''}\Lambda_{jl}^{bc} t_c^k t_a^j \mathcal{R}_{bp''}^{id}\bar{t}_d^l + \bar{\Lambda}_i^a [V^\dagger]_a^i + \bar{\Lambda}_i^a \bar{B}_a^i - \bar{\Lambda}_i^a F_j^i X_a^j + \bar{\Lambda}_i^a \\
&+ \bar{\Lambda}_j^b F_k^j X_{ib}^{ka}\bar{t}_a^i + \bar{\Lambda}_{ja}^{ib} F_i^j \bar{t}_b^k - \bar{\Lambda}_i^a F_j^i X_a^b\bar{t}_b^j + \bar{\Lambda}_i^a B_a^i + \bar{\Lambda}_i^a B_a^{b''}\bar{t}_b^i - \bar{\Lambda}_i^a B_{ja}^{ib}\bar{t}_b^j - \bar{\Lambda}_j^a [\mathcal{R}^\dagger]_{ia}^{bp''} G_{kp''}^{ij} t_b^k + \bar{\Lambda}_i^a [V^\dagger]_a^b t_b^i \\
&+ \bar{\Lambda}_j^c [C^\dagger]_{ic}^{ab} t_{ab}^{ij} + \bar{\Lambda}_k^b [\mathcal{R}^\dagger]_{ib}^{cp''} G_{jp''}^{ia} t_{ac}^{jk} - \bar{\Lambda}_k^c [\mathcal{R}^\dagger]_{ic}^{ap''} G_{jp''}^{kb} t_{ab}^{ij} + \bar{\Lambda}_j^c [V^\dagger]_{ic}^{ab} t_{ab}^{ij} - \bar{\Lambda}_k^a [\mathcal{R}^\dagger]_{ia}^{bp''} G_{jp''}^{ic} t_b^j t_c^k + \bar{\Lambda}_i^a [\mathcal{R} \\
&+ \bar{\Lambda}_j^b [V^\dagger]_{ib}^{ac} t_c^j t_a^i + \bar{\Lambda}_k^c [\mathcal{R}^\dagger]_{jc}^{bp''} G_{ip''}^{ad} t_a^j t_{bd}^{ik} - \bar{\Lambda}_k^b [\mathcal{R}^\dagger]_{jb}^{dp''} G_{ip''}^{ac} t_c^j t_{ad}^{ik} + \bar{\Lambda}_k^a [\mathcal{R}^\dagger]_{ic}^{ap''} G_{jp''}^{bd} t_d^k t_{ab}^{ij} + \bar{\Lambda}_j^c [\mathcal{R}^\dagger]_{kc}^{dp''} G_{ip''}^{ab} t_
\end{aligned}$$

Generalized Contraction Code (GeCCo)

Text art by Mathias Pabst

First git log message: `Thu Mar 15 12:40:33 2007 +0100`

Designed based on ideas gathered from Jeppe Olsen's LUCIA code

Public version at `github.com/ak-ustutt/GeCCo-public`

Disclaimer: Pure development code with (unfortunately) bad documentation and a lot of hot-fixes 🥵

Mainly stand-alone code, integrals from Dalton, Molpro (and everything that provides a `FCIDUMP` file)

Originally intended for:	General-order CC (with selection)
But then used for:	Explicitly-correlated CC
And more lately:	Multireference CC

Contributors:

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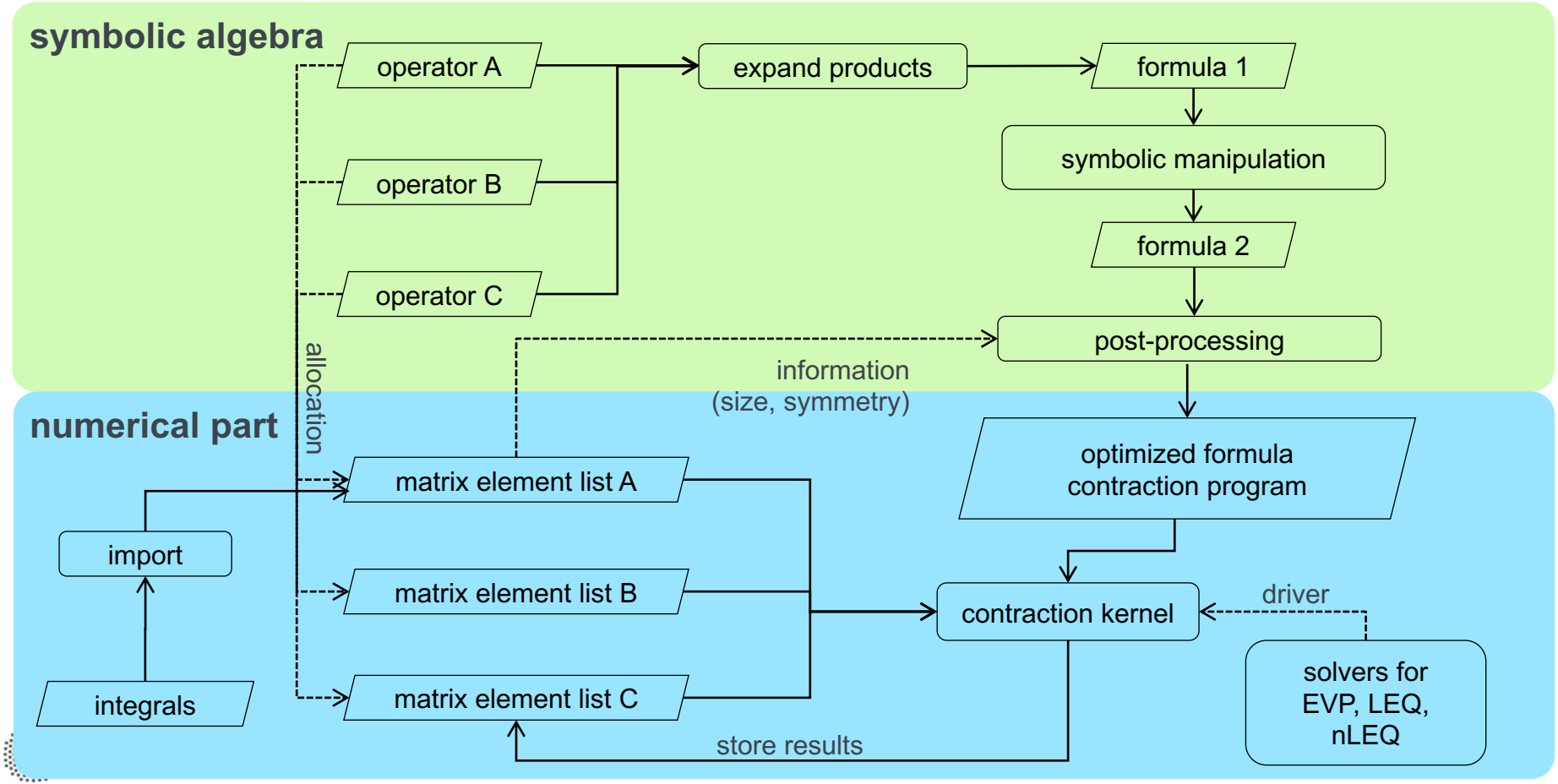
Organization of GeCCo – basic idea



Generating equations: Basic objects

Representation of operators:

$$\hat{T}_2 = \sum_{i,u,a>b} t_{ab}^{iu} \{\hat{a}^a \hat{a}^b \hat{a}_u \hat{a}_i\}$$

name: `T2`

H P V H P V

occupation: `(0,2,0;1,0,1)` or `"PP;HV"`

creations annihilations

$$\hat{H}:$$

$$E_\mathrm{i} = \langle 0|\hat{H}|0\rangle$$

$$\sum_{i,j} f_i^j \{\hat{a}^i \hat{a}_j\}$$

$$\sum_{i>j,u,a} g_{ij}^{au} \{\hat{a}^i \hat{a}^j \hat{a}_u \hat{a}_a\}$$

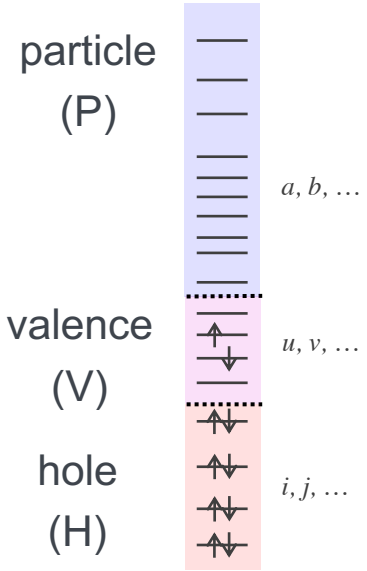
name: `H`

occupation: `(0,0,0;0,0,0)` or `";"`

occupation: `(1,0,0;1,0,0)` or `"H;H"`

occupation: `(2,0,0;0,1,1)` or `"HH;PV"`

“blocks”



inspiration: LUCIA (J. Olsen)

Generating equations: Basic objects

Representation of multiconfigurational state:

$$|\Psi_0\rangle = \sum_{tuvw} C^{(0)}_{tuvw} \{\hat{a}^t \hat{a}^u \hat{a}^v \hat{a}^w\} |0\rangle$$

name: `C0`

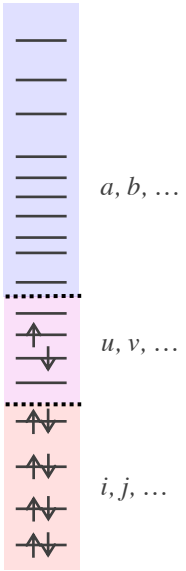
occupation: `(0,0,4;0,0,0)` or `"VVVV;"`

$$\langle\Psi_0| = \sum_{tuvw} \langle 0|\{\hat{a}_w \hat{a}_b \hat{a}_u \hat{a}_t\} C^{(0)}_{tuvw}$$

address as: `C0^+`

occupation (transposed):

`(0,0,0;0,0,4)` or `";VVVV"`



Representation of density matrices:

$$\gamma^{tuv}_{t'u'v'} = \langle\Psi_0|\{\hat{a}^t \hat{a}^u \hat{a}^v \hat{a}_{v'} \hat{a}_{u'} \hat{a}_{t'}\}|\Psi_0\rangle$$
$$= -\langle\Psi_0|\{\hat{a}_{v'} \hat{a}_{u'} \hat{a}_{t'} \hat{a}^t \hat{a}^u \hat{a}^v\}|\Psi_0\rangle$$

occupation:

`(0,0,0;0,0,3|0,0,3;0,0,0)`

or `";VVV|VVV;"`

”double-vertex repr.” (see later)

Generating equations: Operator products

Binary product:

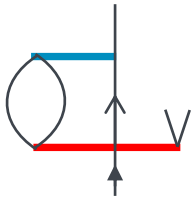
Wick

$$A^{cd}_{ia}\{\hat{a}^i\hat{a}^a\hat{a}_d\hat{a}_c\}B^{jkt}_{efg}\{\hat{a}^e\hat{a}^f\hat{a}^g\hat{a}_t\hat{a}_k\hat{a}_j\} = (C_0)^{jkcdt}_{iaefg}\{\hat{a}^i\hat{a}^a\hat{a}_d\hat{a}_c\hat{a}^e\hat{a}^f\hat{a}^g\hat{a}_t\hat{a}_k\hat{a}_j\} +$$

$$(C_{1,1})^{jkdt}_{iafg}\{\hat{a}^i\hat{a}^a\hat{a}_d\hat{a}_c\hat{a}^e\hat{a}^f\hat{a}^g\hat{a}_t\hat{a}_k\hat{a}_j\} + \ldots$$

$$(C_{3,1})^{jt}_{ag}\{\hat{a}^i\hat{a}^a\hat{a}_d\hat{a}_c\hat{a}^e\hat{a}^f\hat{a}^g\hat{a}_t\hat{a}_k\hat{a}_j\} + \ldots$$

(1,1,0;0,2,0) $[A]$ (0,3,0;2,1,0) $[B]$



Contraction matrix

represent as

	A	B	C
A	(0,0,0;0,0,0)	(1,0,0;0,2,0)	(0,1,0;0,0,0)
B	(0,2,0;1,0,0)	(0,0,0;0,0,0)	(0,1,0;1,0,1)

(0,2,0;1,0,1)

Unique rep. for all topologically equivalent contractions (diagrams) (related to adjacency matrix)

No sign determination at this point

Formalism:

$$[A] = [A]_c + [A]_0 \qquad [B]_c = [A^\dagger]_c$$

$$[B] = [B]_c + [B]_0 \qquad [C] = [A]_0 + [B]_0$$

inspiration: LUCIA (J. Olsen) and M. Kállay's publication on CC eq.s

Generating equations: Operator products

General product of *n* operators:

	A_1	A_2	…	A_n	R	R'
A_1	$[A_1]_1$	$[A_1]_2$	…	$[A_1]_n$	$[A_1]_0$	$[A_1]_{0'}$
A_2	$[A_2]_1$	$[A_2]_2$	…	$[A_2]_n$	$[A_2]_0$	$[A_2]_{0'}$
…	…	…	…	…	…	…
A_n	$[A_n]_1$	$[A_n]_2$	…	$[A_n]_n$	$[A_n]_0$	$[A_n]_{0'}$

> 1 result vertex, if no reordering desired, e.g. for densities:

$$\gamma^{ib}_{aj} \leftarrow \sum_{ck} \lambda^{cb}_{kj} t^{ik}_{ac}$$

Recursive algorithm to determine all possibilities (for given result occupation)

Most frequent case: `(0,0,0;0,0,0)` (i.e. scalar result, “closed diagrams”)

Store result as sequence of contraction matrices (= “formula”)

(+ info on num. prefactor)

Generating equations: Symbolic manipulations

Typical strategy:

Define method via stationary energy functional

$$\mathcal{L} = \langle \Phi_0 | (1 + \hat{\Lambda}) e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle$$

Get working equations as formal derivatives

$$\frac{\partial}{\partial \lambda_\rho} \mathcal{L} = \langle \Phi_0 | \hat{\tau}_\rho^\dagger e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle$$

$$\frac{\partial}{\partial t_\rho} \mathcal{L} = \langle \Phi_0 | (1 + \hat{\Lambda}) [e^{-\hat{T}} \hat{H} e^{\hat{T}}, \hat{\tau}_\rho] | \Phi_0 \rangle$$

Example term:

	LAM	H	T	L
LAM	(0,0,0;0,0,0)	(0,0,0;0,1,0)	(1,0,0;0,0,0)	(0,0,0;0,0,0)
H	(0,1,0;0,0,0)	(0,0,0;0,0,0)	(1,0,0;0,2,0)	(0,0,0;0,0,0)
T	(0,0,0;1,0,0)	(0,2,0;1,0,0)	(0,0,0;0,0,0)	(0,0,0;0,0,0)

	H	T	OMG
H	(0,0,0;0,0,0)	(1,0,0;0,2,0)	(0,1,0;0,0,0)
T	(0,2,0;1,0,0)	(0,0,0;0,0,0)	(0,0,0;1,0,0)

	LAM	H	JT
LAM	(0,0,0;0,0,0)	(0,0,0;0,1,0)	(1,0,0;0,0,0)
H	(0,1,0;0,0,0)	(0,0,0;0,0,0)	(1,0,0;0,2,0)

Generating equations: Further manipulations

- Factor out $R = LH + LHT$ $\xrightarrow{I = H + HT}$ $R = LI$
- Expand $R = LI$ $\xrightarrow{I = H + HT}$ $R = LH + LHT$
- Transpose $HT + T^\dagger HT$ $\longrightarrow$ $T^\dagger H + T^\dagger HT$
- Sum up $HT + T^\dagger HT - T^\dagger H - T^\dagger HT$ $\longrightarrow$ $HT - T^\dagger H$

Generating equations: Input language

`make` inspired work-flow driver:

define targets, dependencies, rules (= command sequences)

V0: hard-coded

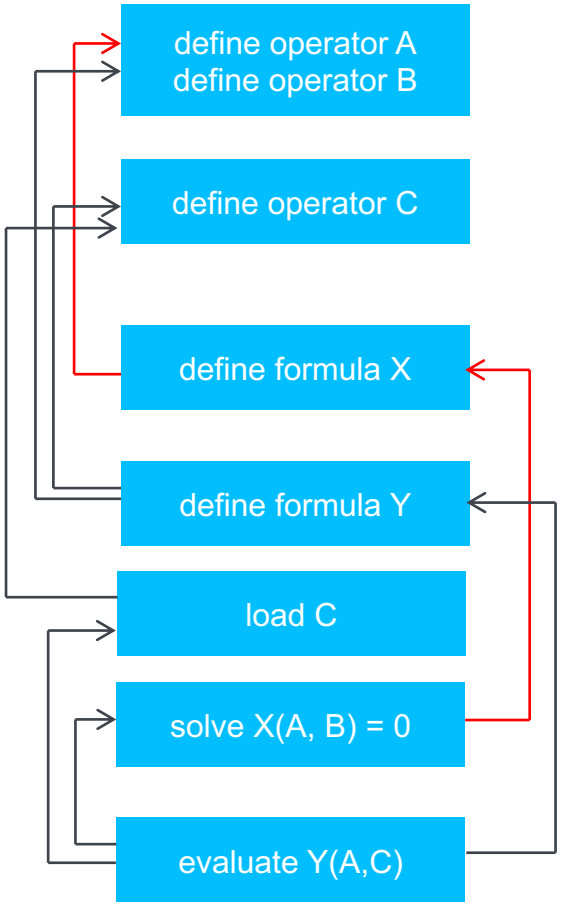
V1: simple self-written parser

V2: use Python as input parser (allow additional logic)

V2a: Python-based parsing of equation strings

Note: Python parsing only at initial input read-in

Conversion to input for Fortran, actual program is purely Fortan90 (and sometimes beyond)



Generating equations: Input language example

```
# Operators ------------------------------------
new_target('CCD_OPS')
DEF_SCALAR({LABEL:'LCCD'})
DEF_SCALAR({LABEL:'ECCD'})
DEF_EXCITATION({LABEL:'T2',MIN_RANK:2,MAX_RANK:2})
CLONE_OPERATOR({LABEL:'O2',TEMPLATE:'T2'})
CLONE_OPERATOR({LABEL:'L2',TEMPLATE:'T2',ADJOINT:True})

# CC Lagrangian --------------------------------
new_target('CCD_LAG')
depend('H')
depend('CCD_OPS')
form_l1 = stf.Formula("CCD_LAG:LCCD=<H+[H,T2]>")
form_l1.append("<L2*(H+[H,T2]+0.5*[[H,T2],T2])>")
form_l1.set_rule()
PRINT_FORMULA({LABEL:'CCD_LAG',MODE:'SHORT'})
```

$$\hat{T}_2$$

$$\Omega_2 = \langle \Phi_0 | \hat{a}_{ab}^{ij} \bar{H} | \Phi_0 \rangle$$

$$\hat{\Lambda}_2$$

$$\mathcal{L} = \langle \Phi_0 | (1 + \hat{\Lambda}_2) e^{\cdot \hat{T}_2} \hat{H} e^{\hat{T}_2} | \Phi_0 \rangle$$

$$= \langle \Phi_0 | \hat{H} + [\hat{H}, \hat{T}_2] | \Phi_0 \rangle$$

$$+ \langle \Phi_0 | \hat{\Lambda}_2 (\hat{H} + [\hat{H}, \hat{T}_2] + \frac{1}{2}[[\hat{H}, \hat{T}_2], \hat{T}_2]) | \Phi_0 \rangle$$

Generating equations: Input I

```
# Operators ----------------------------------
new_target('CCD_OPS')
DEF_SCALAR({LABEL:'LCCD'})
DEF_SCALAR({LABEL:'ECCD'})
DEF_EXCITATION({LABEL:'T2',MIN_RANK:2,MAX_RANK
CLONE_OPERATOR({LABEL:'O2',TEMPLATE:'T2'})
CLONE_OPERATOR({LABEL:'L2',TEMPLATE:'T2',ADJOI

# CC Lagrangian ------------------------------
new_target('CCD_LAG')
depend('H')
depend('CCD_OPS')
form_l1 = stf.Formula("CCD_LAG:LCCD=<H+[H,T2]>")
form_l1.append("<L2*(H+[H,T2]+0.5*[[H,T2],T2])>")
form_l1.set_rule()
PRINT_FORMULA({LABEL:'CCD_LAG',MODE:'SHORT'})

# CC E and Residual --------------------------
new_target('CCD_E_R')
depend('CCD_LAG')

DERIVATIVE({LABEL_RES:'CCD_R',LABEL_IN:'CCD_LAG',
            OP_RES:'O2',OP_DERIV:'L2'})
INVARIANT({LABEL_RES:'CCD_E',LABEL_IN:'CCD_LAG',
            OP_RES:'ECCD',OPERATORS:['L2']})
```

```
 1 LCCD(1) <-  1.000000 H(1)
 2 LCCD(1) <-  1.000000 H(8) T2(1) [1,2,HH,PP]
 3 LCCD(1) <-  1.000000 L2(1) H(12) [1,2,HH,PP]
 4 LCCD(1) <-  1.000000 L2(1) H(2) T2(1) [1,2,H,][1,3,H,PP][2,3,H,]
 5 LCCD(1) <-  1.000000 L2(1) H(5) T2(1) [1,2,,P][1,3,HH,P][2,3,,P]
 6 LCCD(1) <-  1.000000 L2(1) H(6) T2(1) [1,2,HH,][1,3,,PP][2,3,HH,]
 7 LCCD(1) <-  1.000000 L2(1) H(10) T2(1) [1,2,H,P][1,3,H,P][2,3,H,P]
 8 LCCD(1) <-  1.000000 L2(1) H(14) T2(1) [1,2,,PP][1,3,HH,][2,3,,PP]
 9 LCCD(1) <-  1.000000 L2(1) H(8) T2(1) T2(1) [1,3,H,][2,3,H,PP][1,4,H,PP][2,4,H,]
10 LCCD(1) <-  1.000000 L2(1) H(8) T2(1) T2(1) [1,3,HH,][2,3,,PP][1,4,,PP][2,4,HH,]
11 LCCD(1) <-  1.000000 L2(1) H(8) T2(1) T2(1) [1,3,,P][2,3,HH,P][1,4,HH,P][2,4,,P]
12 LCCD(1) <-  0.500000 L2(1) H(8) T2(1) T2(1) [1,3,H,P][2,3,H,P][1,4,H,P][2,4,H,P]
```

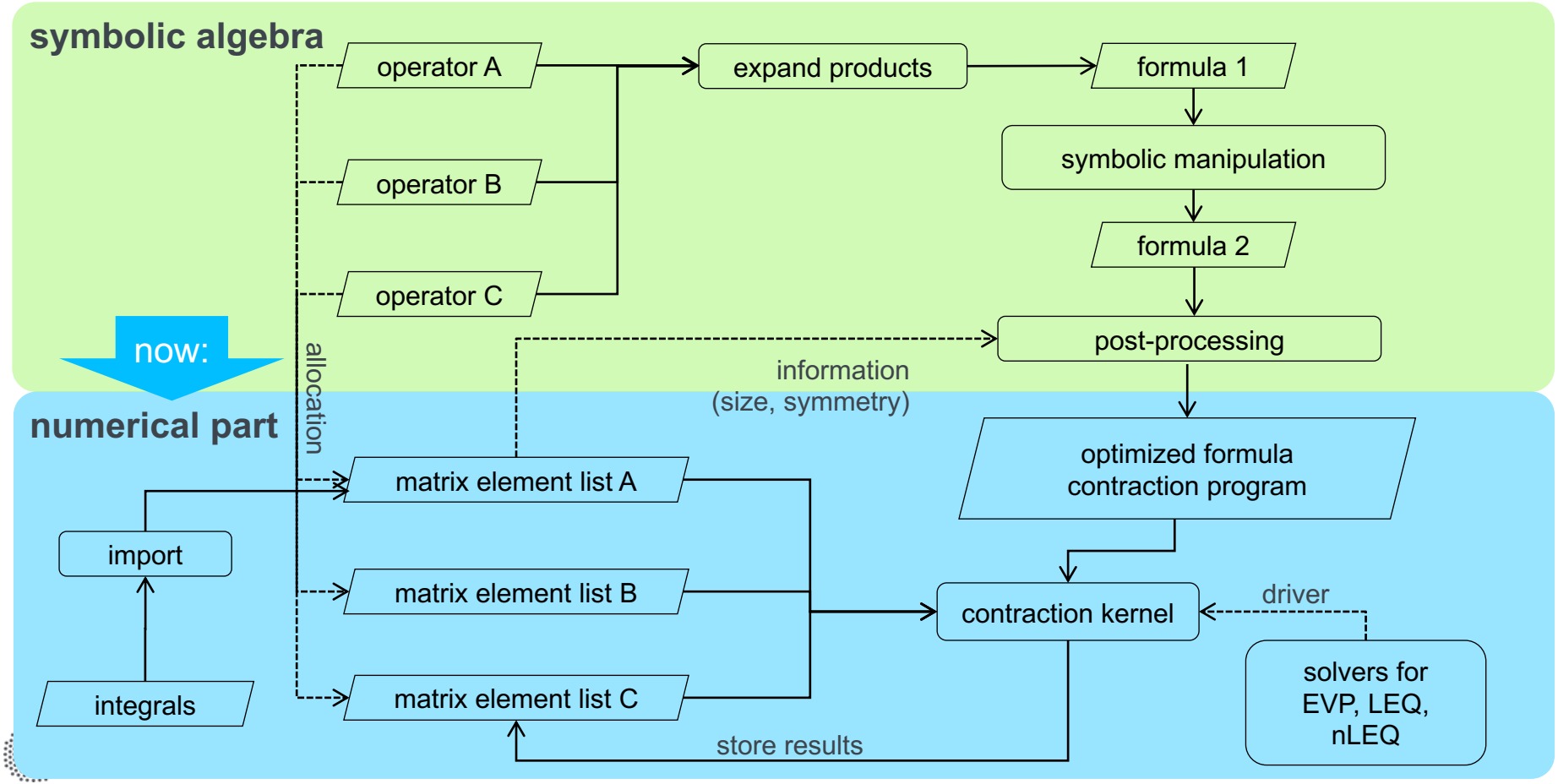
$$\mathcal{L} = \langle \Phi_0 | (1 + \hat{\Lambda}_2) e^{\cdot \hat{T}_2} \hat{H} e^{\hat{T}_2} | \Phi_0 \rangle$$

$$= \langle \Phi_0 | \hat{H} + [\hat{H}, \hat{T}_2] | \Phi_0 \rangle$$

$$+ \langle \Phi_0 | \hat{\Lambda}_2 (\hat{H} + [\hat{H}, \hat{T}_2] + \frac{1}{2}[[\hat{H}, \hat{T}_2], \hat{T}_2]) | \Phi_0 \rangle$$

$$(\Omega_2)^{ij}_{ab} = \frac{\partial \mathcal{L}}{\partial \lambda^{ij}_{ab}}$$

Organization of GeCCo – basic idea



Towards numerical evaluation: Optimizations

Strength reduction → binary contractions

$$\sum_{cdkl} g_{kl}^{cd} t_{ab}^{ik} t_{cd}^{jl} = \sum_{k} \left(\sum_{cdl} g_{kl}^{cd} t_{cd}^{jl} \right) t_{ab}^{ik}$$

Common subexpression identification (recursive intermediate fact.)

$$\sum_{k} f_{j}^{k} t_{ab}^{ik} + \sum_{k} \left(\sum_{cdl} g_{kl}^{cd} t_{cd}^{jl} \right) t_{ab}^{ik} = \sum_{k} \left(f_{j}^{k} + \sum_{cdl} g_{kl}^{cd} t_{cd}^{jl} \right) t_{ab}^{ik}$$

not coupled here

Alternative: Pre-define intermediates (not automated)

➡ Optimized list of binary contractions

Towards numerical evaluation: Tensor contraction kernel

external indices

$$R^{ij}_{ab} \leftarrow \sum_{kld} g^{jd}_{kl} t^{ikl}_{abd}$$

contraction indices

General scheme:

$$A(\mathcal{K}) \rightarrow A(\mathcal{C}, \mathcal{K}_0)$$
$$B(\mathcal{L}) \rightarrow B(\mathcal{C}^\dagger, \mathcal{L}_0)$$
$$R(\mathcal{K}_0, \mathcal{L}_0) = A(\mathcal{C}, \mathcal{K}_0) B(\mathcal{C}^\dagger, \mathcal{L}_0)$$
$$R(\mathcal{K}_0, \mathcal{L}_0) \rightarrow R(\mathcal{I})$$

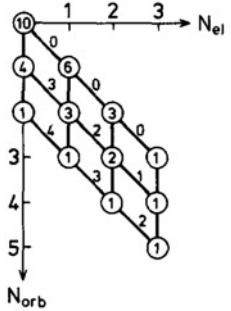
Address string is composed of substrings:

$$\mathcal{K} = \mathcal{K}^{\mathrm{c}}_{\mathrm{H}} \mathcal{K}^{\mathrm{c}}_{\mathrm{P}} \mathcal{K}^{\mathrm{c}}_{\mathrm{V}} \mathcal{K}^{\mathrm{a}}_{\mathrm{H}} \mathcal{K}^{\mathrm{a}}_{\mathrm{P}} \mathcal{K}^{\mathrm{a}}_{\mathrm{V}}$$

Generate unique flat index for substrings:

String resolutions come with sign changes and increased sparsity (unpacking):

$$(ij) \rightarrow \begin{matrix} 0 & + & + & + \\ - & 0 & + & + \\ - & - & 0 & + \\ - & - & - & 0 \end{matrix}$$



Batched unpacking, use sparsity in outer loops, innermost loops use `dgemm`

Olsen, Roos, Jørgensen, Jensen, JCP **89**, 2185 (1988)

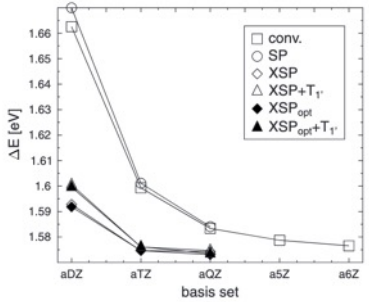
Kállay, Surján, JCP **115**, 2945 (2001)

Application examples

F12 theory

Complete basis correction

$$\exp(\hat{T}_1 + \hat{T}_2 + \hat{T}_{2'})|\Phi_0\rangle \qquad \hat{T}_{2'} = \sum_{i>j,k>l,\alpha>\beta} c_{kl}^{ij} \langle \alpha\beta|\hat{Q}_{12} f(r_{12})|kl\rangle \hat{a}_{kl}^{\alpha\beta}$$



Comment on Quintuple-ζ quality coupled-cluster correlation energies with triple-ζ basis sets by D. P. Tew, W. Klopper, C. Neiss and C. Hättig, *Phys. Chem. Chem. Phys.*, 2007, 9, 1921 [erratum]

David P. Tew,[a] Wim Klopper,*[a] Christian Neiss[b] and Christof Hättig[c]

Received 7th July 2008, Accepted 18th July 2008
First published as an Advance Article on the web 15th September 2008
DOI: 10.1039/b811567b

erroneous values. Our current implementation is in complete agreement with an independently programmed CCSD(F12) program that uses generalised contraction routines[2] and we are certain that the values reported here are reliable. The

2 A. Köhn and G. Richings, private communication.

$$\exp(\hat{T}_1 + \hat{T}_2 + \hat{R} + [\hat{R}, \hat{T}_1 + \hat{T}_2])|\Phi_0\rangle$$

"Full" CCSD-F12

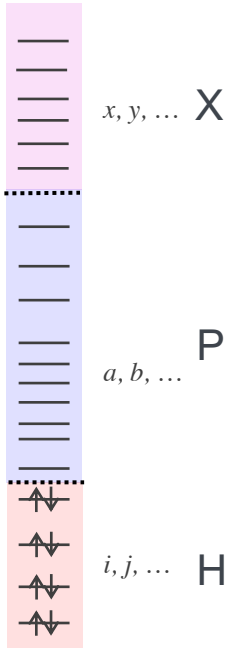
AK, Richings, Tew, JCP 129, 201103 (2008)
Shiozaki, Kamiya, Hirata, Valeev, JCP 129, 071101 (2008)
AK, Tew, JCP 133, 174117 (2010)

Explicitly-correlated triple excitations

AK, JCP 130, 131101 (2009)
AK, JCP 133, 174118 (2010)

CCSD-F12 response theory

AK, JCP 130, 104104 (2009)
Hanauer, AK, JCP 131, 124118 (2009)



Application examples

Multireference coupled-cluster theory

$$|\Psi\rangle = e^{\hat{T}}|\psi_0\rangle = e^{\hat{T}} \sum_{\mu} |\Phi_\mu\rangle c_\mu$$

$$|\Psi_0\rangle = \sum_{tuvw} C^{(0)}_{tuvw} \{\hat{a}^t \hat{a}^u \hat{a}^v \hat{a}^w\} |0\rangle$$

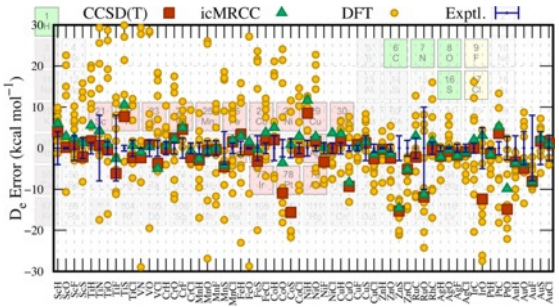
Evangelista, Gauss, JCP 134, 114102 (2011)
Hanauer, Köhn, JCP 134, 204111 (2011)

Interesting features:

Spin-adapted, strong analogy to single-reference theory, orbital invariance

But: Very complex eq.s

Benchmarking transition metal bond energies



Aoto, Lima Batista, AK, Oliveira-Filho, JCTC 13, 5291 (2017)

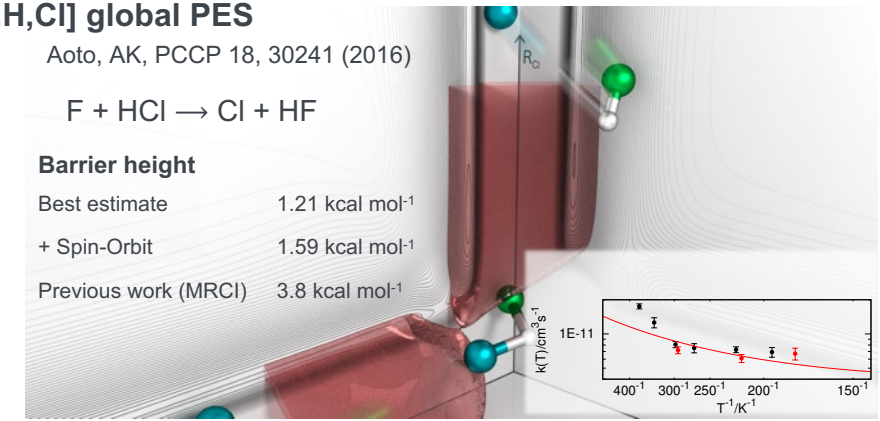
[F,H,Cl] global PES

Aoto, AK, PCCP 18, 30241 (2016)

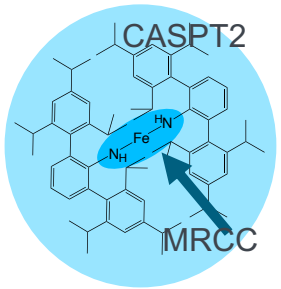
F + HCl ⟶ Cl + HF

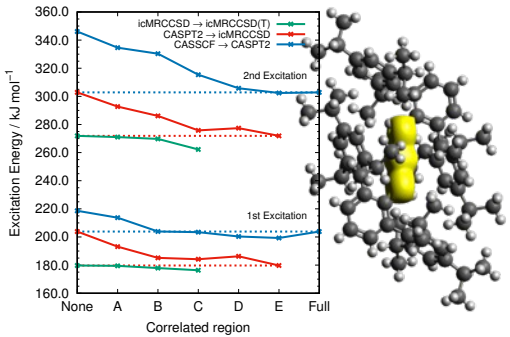
Barrier height

Best estimate	1.21 kcal mol^{-1}
+ Spin-Orbit	1.59 kcal mol^{-1}
Previous work (MRCI)	3.8 kcal mol^{-1}



Larger systems by embedding





Coughtrie, Giereth, Kats, Werner, AK, JCTC 14, 693 (2018)

Improving numerical evaluation: Translation

GeCCo's numerics are not bad, but certainly not good enough for routine applications

Couple to a more efficient tensor evaluation framework: ITF (Knizia, Shamasundar, Kats)

Encode algorithm in meta-language

```
tensor: R[aaii], !Create{type:disk; sym:01/23}, ResT2

. . .

for [k,j]:
   .R[abkj] += K[abkj]

   load K4E[abkj]
   .R[abkj] += K4E[abkj]
   drop K4E[abkj]

   alloc C[abkj]
   .C[abkj] += T[abkj]
   .C[abkj] += t[ak] t[bj]
   .R[abmn] += C[abkj] A[mnkj]
   drop C[abkj]
```

Hand-written code
Some optimization by Ch. Köppl, PhD-thesis

Uses intrinsic features of Molpro

integral-direct two-electron transformations

$$\frac{1}{2}\sum_{cd} g_{ab}^{cd}\left(t_{cd}^{ij} + t_c^i t_d^j\right)$$

coupling coefficients and densities for internally contracted theories

Shamasundar, Knizia, Werner, JCP **135**, 054101 (2011)
Kats, Manby, JCP **138**, 144101 (2013)

Improving numerical evaluation: Translation

Use pre-optimized sequence of binary contractions from GeCCO, translate to ITF code

Josh A. Black

Main issues: GeCCo is spin-orbital string based

- Must work out spin summation and explicit labels + signs
- Post-processing to meet ITF syntax (declarations etc.)
- Write new C++ driver code

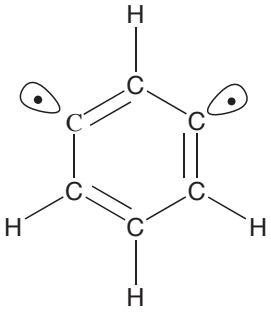
$$\sum_{vw} \gamma_w^v \sum_{abi} g_{iv}^{ab} t_{ab}^{iw}$$

$$\sum_{vw} \Gamma_w^v \sum_{abi} K_{iv}^{ab} (2T_{ab}^{iw} - T_{ba}^{iw})$$

Current status: Only CAS(2,2), only partial spin summation and no optimal factorization of non-linear terms

Black, Waigum, Adam, Shamasundar, AK, JCP **158**, 134801 (2023)

Performance



singlet state
CAS(2,2)

Approximation with linearization of “difficult terms” (many active space indices)

Parallelization: Too granular code currently, embarrassingly parallel tasks (Gradients, Hessian) work well

integral trafo + resort

Method (Impl.)	Basis set	Overhead [s]	Time/iter [s]	# iter
icMRCCSD (GeCCo)	cc-pVDZ	56	42	20
	cc-pVTZ	1282	441	21
icMRCCSD (ITF)	cc-pVDZ	0.7	10	21
	cc-pVTZ	3	68	20
	cc-pV5Z	238	3872	20
icMRCC/CEPA (ITF)	cc-pVTZ	3	5	31
	cc-pV5Z	237	251	31
CCSD (Molpro)	c-pVTZ	1	1.7	16
	cc-pV5Z	190	142	16

#bf: 104 (cc-pVDZ), 236 (cc-pVTZ), 766 (cc-pV5Z)

Black, Waigum, Adam, Shamasundar, AK, JCP **158**, 134801 (2023)

Future aims

GeCCo → Lizard `github.com/KoehnLab/Lizard`

Goals: Term generation features of GeCCo + code generation for tensor engines

Robert Adam

More modularity (or: less monolithic)

(interfaces to other term generators,
other tensor contraction kernels)

Python interface for input control and fast prototyping

Improvements, like:

- Generalization of index spaces (e.g. for tensor decompositions)
- More global representation of terms (expression trees)
- New treatment of index permutations

Future aims

In fact there are many related projects (Quantum Chemistry focus, as collected by Robert):

- Early work by Janssen & Schaefer [1]
- TCE (Hirata et al. [2])
- SMITH (Shiozaki et al. [3])
- ACE (Song et al. [4])
- MRCC (Kállay et al. [5])
- Orca-AGE (Krupika et al. [6])
- GeCCo (Köhn et al. [7])
- SeQuant (by Valeev group)
- drudge (Zhao [8])
- Cadabra (Peeters [9]; v2: Peeters [10])
- Datta & Gauss [11]
- MacLeod & Shiozaki [12]
- ITF (Molpro [13])
- squant (Kats)
- SIAL (ACES III [14])
- CTF (Solomonik et al. [15])
- libtensor (Epifanovsky et al. [16])
- tiledarray (Peng et al. [17])

Future aims

Brainstorming: How could we all better interact?

Some standard(s) to store generated equations?

Some API standard(s) for tensor contraction engines?

Review paper on best practices?

Some references for slide 24

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